

NEUTRON DIFFRACTION STUDIES OF TRANSITION METAL HYDRIDE COMPLEXES*

Thomas F. Koetzle
 Chemistry Department, Brookhaven National Laboratory
 Upton, New York 11973

Robert Bau
 Department of Chemistry, University of Southern California
 Los Angeles, California 90007

ABSTRACT

The first neutron diffraction study of a transition metal hydride complex was that of $[\text{HgRe}]^{2-}$ (I), reported in 1964, followed by $\text{HMn}(\text{CO})_5$ (II) in 1969. Recently, a number of other hydride complexes have been studied at Brookhaven. Thus far, investigations of $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2^-$ (III), $\text{HW}_2(\text{CO})_9(\text{NO})$ (IV), and $\text{HW}_2(\text{CO})_8(\text{NO})(\text{P}(\text{OCH}_3)_3)$ (V) have been completed. Preliminary results are available for $\text{HFeCo}_3(\text{CO})_9[\text{P}(\text{OCH}_3)_3]_3$ (VII). This work, together with studies of $\text{HMn}_2(\text{C}_5\text{H}_5)_2(\text{CO})_4(\text{P}(\text{CH}_3)_2)$ (VI) and $[(\text{C}_2\text{H}_5)_4\text{N}]^+[\text{HCr}_2(\text{CO})_{10}]^-$ carried out at Argonne has led to some general observations on the geometry and the nature of bonding in these compounds. For example, in the structures of IV and V, both of which have bent W-H-W linkages ($\angle \text{W}-\text{H}-\text{W}$ in the range $125-130^\circ$), there is conclusive evidence for the existence of a closed three-center W-H-W bond with significant metal-metal interaction. Such is the case, because extensions of the axial W-C and W-N bonds trans to the hydride intersect at a point near the center of the W-H-W triangle. The geometry of VI, which also contains a bent M-H-M bond, is consistent with that of IV and V. Bridging M-H bonds in these second- and third-row hydrides range in length from 1.85 to 1.89 Å, compared to 1.75 Å in the first-row polynuclear complex VII. For metals of corresponding rows, bridging M-H bonds are about 0.1 Å longer than terminal bonds, which are classified as single covalent bonds.

INTRODUCTION

The chemistry of hydride complexes of the transition metals has developed rapidly in the past twenty years.¹ The nature of bonding between metal and hydrogen in these compounds is of great general interest.

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Hydride complexes have practical as well as theoretical importance. For example, several complexes have applications as hydrogenation catalysts. In addition, polynuclear hydrides may provide models for bonding of hydrogen to active-metal surfaces.

In order to understand the stereochemistry in metal hydride complexes, it is necessary to determine reliable hydrogen atom positions. In some cases, hydrogen atoms have been located and even refined from x-ray diffraction data, but these positions are subject to large uncertainties and systematic errors, particularly in structures which contain heavy elements. In general, neutron diffraction is the only technique for obtaining accurate hydrogen atom positions in complicated structures, and in fact it was only with the advent of neutron diffraction that details of the bonding of hydrogen in metal hydride complexes began to be well understood.²

The first neutron diffraction study of a transition metal hydride complex was that of the potassium salt of $[\text{H}_9\text{Re}]^{2-}$ (I)³, reported in 1964, followed by $\text{HMn}(\text{CO})_5$ (II)⁴ and $\text{HZN}(\text{CH}_3)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$ ⁵ in 1969. The study of $\text{HMn}(\text{CO})_5$ demonstrated unequivocally that hydrogen in II is a stereochemically active ligand, and the metal-hydrogen distances found in all three complexes correspond to normal covalent bonds. Recently, a number of additional hydride complexes have been studied at Brookhaven. The results of these investigations together with other recent studies carried out at Argonne and Harwell are discussed below.

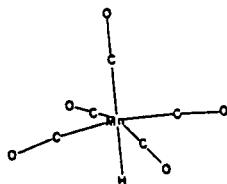
COMPLEXES WITH A SINGLE METAL

Five structures have been completed in this group to date. In ad-

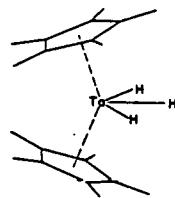
dition to the above-mentioned investigations of I and II* and of $\text{H}_2\text{ZnN}-(\text{CH}_3)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$, structures of two bent bis- π -cyclopentadienyl complexes have been determined. Studies have been carried out at Brookhaven on $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$ (III)⁶ at 91 and 298 K, and at Harwell on $\text{D}_2\text{Mo}(\text{C}_5\text{H}_5)_2$.⁷



I



II



III

Anion I is found to have essentially D_{3h} symmetry, with a mean Re-H bond distance of 1.68 Å. The hybridization on Re may be assigned as $d^5 s^3$. Compound II exists in two crystalline forms. An x-ray study of the α -form⁸ did not locate the hydride, but showed the molecule to have essentially C_{4v} symmetry, and indicated that the hydride occupies a normal coordination site. A neutron diffraction study of the β -form confirmed this molecular structure and showed the Mn-H bond distance to be 1.60(2) Å**, or approximately that expected for a normal covalent bond.

* Illustrations were adapted from scaled drawings prepared on a PDP11/40 - Vector General 3D2 graphics system, with program PRJCTN by L. E. McCandlish, L. C. Andrews and H. J. Bernstein (see T. F. Koetzle, L. C. Andrews, F. C. Bernstein, and H. J. Bernstein in "Computer Networking and Chemistry," P. Lykos, Ed., American Chemical Society, Washington, D. C., 1975, p. 1).

** Estimated standard deviations are given in parentheses in units of the least-significant digit.

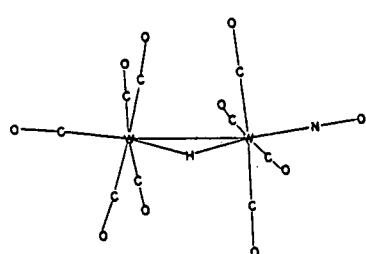
The zinc complex $\text{HZN}(\text{CH}_3)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$ crystallizes as a dimer, with a four-membered Zn_2N_2 ring, and the terminal $\text{Zn}-\text{H}$ distance was found to be 1.60 \AA . Neither atomic coordinates nor estimated standard deviations of bond distances have been reported for this compound.

$\text{D}_2\text{Mo}(\text{C}_5\text{H}_5)_2$ is a simple example of a class of bent bis- π -cyclopentadienyl complexes $\text{L}_2\text{M}(\text{C}_5\text{H}_5)_2$, and compound III falls in the class $\text{L}_3\text{M}(\text{C}_5\text{H}_5)_2$. Lauher and Hoffmann recently have systematically studied⁹ the bonding in such complexes, within the framework of extended-Hückel (EH) MO theory. Their EH treatment delineates three frontier orbitals available to bond to the ligands L, quite similar to those deduced on qualitative grounds by Green et al,¹⁰ and clarifies the relationship between the contrasting hybridization schemes of Ballhausen and Dahl¹¹ and Alcock.¹² These latter schemes are equivalent to taking different linear combinations of the frontier orbitals. In agreement with EPR results,¹³ EH theory predicts the unpaired electron in a d^1 complex of type $\text{L}_2\text{M}(\text{C}_5\text{H}_5)_2$ to be directed along the normal to the line bisecting $\rangle \text{L}-\text{M}-\text{L}$, as predicted in the Alcock model, rather than parallel to this line, as in the Ballhausen-Dahl model. Normal σ -bonds are expected to the hydride ligands in $\text{D}_2\text{Mo}(\text{C}_5\text{H}_5)_2$ and in III. Observed distances in the neutron diffraction studies are 1.96 \AA for $\text{Mo}-\text{D}$ and 1.75 \AA for $\text{Ta}-\text{H}$. This Mo-D distance seems abnormally long, and may be subject to fairly large uncertainty. The data were obtained by profile analysis of a neutron powder diffraction pattern and the cyclopentadienyl rings did not appear well-behaved in the structure refinement.⁷ All three Ta-H bonds in III are of equal length, while in an x-ray diffraction study of the related $\text{H}_3\text{Nb}(\text{C}_5\text{H}_5)_2$ ⁶ the central Nb-H bond is found to be longer than the

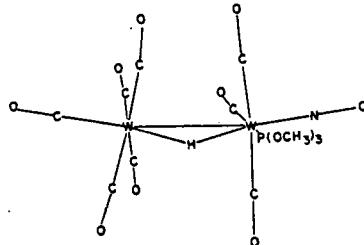
exterior bonds (1.9(1) vs. 1.6(1) Å). An EH calculation on $[\text{H}_3\text{Ti-}(\text{C}_5\text{H}_5)_2]^-$ predicts an overall $\angle \text{H-M-H}$ of 129° , which agrees quite well with the observed value in III of 125° . The $\angle \text{D-Mo-D}$ of 83° found in $\text{D}_2\text{Mo}(\text{C}_5\text{H}_5)_2$ is similar to that found in several other $d^2 \text{L}_2\text{M}(\text{C}_5\text{H}_5)_2$ complexes, as tabulated by Prout et al.⁷

BINUCLEAR COMPLEXES

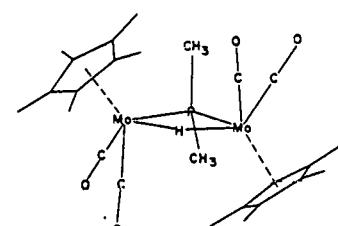
Thus far, studies have been completed on three binuclear complexes, all of which contain a hydride ligand bridging two identical metal atoms: $\text{HW}_2(\text{CO})_9(\text{NO})$ (IV),¹⁴ $\text{HW}_2(\text{CO})_8(\text{NO})(\text{P}(\text{OCH}_3)_3)$ (V),¹⁵ and $\text{HMn}_2(\text{C}_5\text{H}_5)_2(\text{CO})_4(\text{P}(\text{CH}_3)_2)$ (VI).¹⁶ The first two studies were carried



IV



V



VI

out at Brookhaven and the latter at Argonne. The investigations of IV and V were undertaken to answer fundamental questions regarding the nature of bent M-H-M bonds, viz. (a) Are such bonds inherently asymmetric or can they be symmetric in certain cases? (b) Are the three-center two-electron M-H-M bonds of the closed variety, with some M-M overlap or are they open with no appreciable M-M interaction? The results point conclusively to the existence of closed W-H-W bonds in IV and V. Such is the case, because extensions of the axial W-C and W-N bonds trans to the hydride intersect at a point near the center of the

W-H-W triangle. The structure of VI, which contains a second bridging $\text{P}(\text{CH}_3)_2$ ligand, is consistent with that of IV and V. Geometrical details for M-H-M bonds in these structures are summarized in Table 1.

Table 1. Summary of Neutron Diffraction

Results on Bent M-H-M Bonds

Compound		$\text{M}-\text{H}(\text{\AA})$	$\text{M}-\text{H}-\text{M}$ (deg.)	$\text{M}-\text{M}(\text{\AA})$	Reference
$\alpha\text{-HW}_2(\text{CO})_9(\text{NO})$	IV	1.875(4) 1.876(4)	125.0(2)	3.328(3)	14
$\beta\text{-HW}_2(\text{CO})_9(\text{NO})$	IV	1.870(4)	125.9(4)	3.330(3)	14
$\text{HW}_2(\text{CO})_8(\text{NO})(\text{P}(\text{OCH}_3)_3)$	V	1.859(7) 1.894(6)	129.4(3)	3.393(4)	15
$\text{HMo}_2(\text{C}_5\text{H}_5)_2(\text{CO})_4(\text{P}(\text{CH}_3)_2)$	VI	1.851(4) 1.869(4)	122.9(2)	3.267(2)	16

The W-H-W bond in V is found to be slightly asymmetric (the difference between the two W-H distances is 0.035(10) \AA) with the hydrogen displaced toward the $\text{W}(\text{CO})_5$ unit. The direction of displacement is consistent with effective atomic number rule (EAN) considerations, as the $\text{W}(\text{CO})_5$ group is the more electron deficient portion of the molecule. It was impossible to discriminate between a symmetric and an asymmetric bridge in the structure of either crystalline form of IV, since in both forms the molecule is disordered, by means of rotation about the pseudo two-fold axis passing through the hydrogen.

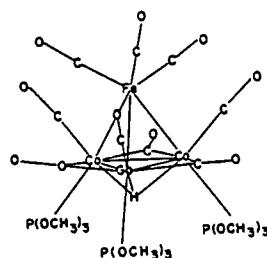
The anion $[\text{HW}_2(\text{CO})_{10}]^-$ has been studied by x-ray diffraction¹⁷ in the structures of two salts with different counterions: $[(\text{C}_2\text{H}_5)_4\text{N}]^+$ and $[(\text{C}_6\text{H}_5)_3\text{P})_2\text{N}]^+$ or PPN^+ . In the PPN^+ salt, the anion has a structure very similar to that of IV and V, and almost certainly contains a bent, symmetric W-H-W bridge, although the hydrogen atom was not located. The $[(\text{C}_2\text{H}_5)_4\text{N}]^+$ salt, in which the anion has D_{4h} symmetry, is isostructural with $[(\text{C}_2\text{H}_5)_4\text{N}]^+ [\text{HCr}_2(\text{CO})_{10}]^-$. This chromium complex had been postulated to contain a linear Cr-H-Cr bridge,¹⁸ but a recent neutron diffraction study carried out at Argonne indicates¹⁹ a disordered structure with two hydrogen sites of 50 per-cent occupancy, displaced off the Cr-Cr axis, such that the $\angle \text{H-Cr-Cr}$ is $21.1(6)^\circ$. The half-hydrogen atoms are located almost exactly mid-way between the two chromium atoms, with H-Cr distances of $1.74(2)$ and $1.71(2)$ Å.

The W-W distance in $[(\text{C}_2\text{H}_5)_4\text{N}]^+ [\text{HW}_2(\text{CO})_{10}]^-$ is $3.504(1)$ Å, or 0.25 Å shorter than twice the W-H bridging distance found in IV and V. This observation may be explained if we suppose that it is not the W-H bond length but the W-W overlap distance which remains fairly constant. This distance is estimated as the distance from the tungsten atom to the center of the W-H-W triangle in IV and V, or 1.75 Å. This is almost precisely half the W-W distance found in $[(\text{C}_2\text{H}_5)_4\text{N}]^+ [\text{HW}_2(\text{CO})_{10}]^-$, where the linear arrangement of bonds to the axial carbonyl ligands requires that the tungsten orbitals which bond to hydrogen must lie along the W-W axis.

POLYNUCLEAR COMPLEXES

Preliminary neutron diffraction results are available for one

polynuclear complex: $\text{HFeCo}_3(\text{CO})_9[\text{P}(\text{OCH}_3)_3]_3$ (VII).²⁰ This investigation confirms the location in an x-ray study²¹ of the hydrogen atom



VII

triply bridging the cobalt atoms, and in a position displaced 0.75 Å from the plane through these atoms, on the side opposite the iron atom. The hydrogen atom is found by neutron diffraction to be located essentially on the three-fold molecular axis, with a mean Co-H distance of 1.75 Å.

In conclusion, to date structures of ten transition metal hydride complexes have been studied by neutron diffraction. Based upon the results now available, it is reasonable to estimate that for bent M-H-M bridges ($\angle \text{M}-\text{H}-\text{M} \approx 120^\circ - 130^\circ$) in second- and third-row hydride complexes, M-H bonds will range in length from 1.8 to 1.9 Å, while terminal M-H bonds will generally be 0.1-0.2 Å shorter. This difference corresponds formally to a decreased bond order in bridging bonds. Both bridging and terminal M-H bonds in first-row hydrides are expected to be about 0.1 Å shorter than those in second- and third-row complexes.

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